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ASD-TDR-62-1025
VOLUME II of V

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FINAL REPORT FOR HIGH ENERGY FUELS PROJECT
VOLUME II. THEORY OF DIBORANE PYROLYSIS

TECHNICAL DOCUMENTARY REPORT NR. ASD-TDR-62-1025. VOLUME II

JUNE 1962

CHEMICAL ENGINEERING BRANCH
MANUFACTURING TECHNOLOGY LABORATORY
AERONAUTICAL SYSTEMS DIVISION
AIR FORCE SYSTEMS COMMAND
UNITED STATES AIR FORCE
WRIGHT-PATTERSON AIR FORCE BASE, OHIO

ASD PROJECT NR. 7-558b

Prepared Under Contract AF 33(600)-35745

AFN, Inc.
LOS ANGELES 5, CALIFORNIA
Author Dr. T. W. Clapper

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FOREWORD

Volume Two of this Final Technical Documentary Report covers all work performed on the theory of diborane pyrolysis under Contract AF 33(600)-35745 from September 1957 to March 1962. The manuscript was released by the author on 15 June 1962 for publication as an ASD Technical Documentary Report.

This contract with AFN, Inc., comprised of American Potash & Chemical Corporation, FMC Corporation, and National Distillers and Chemical Corporation, with main offices located in Los Angeles, California, was initiated under Manufacturing Methods Project 7-558b, "High Energy Fuels Project." It was accomplished under the technical direction of Mr. Charles Tanis, Chemical Engineering Branch (ASRCTC), Manufacturing Technology Laboratory, Aeronautical Systems Division, Wright-Patterson Air Force Base, Ohio.

Dr. T. W. Clapper of American Potash & Chemical Corporation was Project Manager. The work covered in Volume Two was performed in the Whittier, California Laboratory of American Potash & Chemical Corporation by R. D. Stewart and R. G. Adler.

This project has been carried out as part of the Air Force Manufacturing Methods Program. The primary objective of the Air Force Manufacturing Methods Program is to develop on a timely basis manufacturing processes, techniques and equipment for use in economical production of USAF materials and components. This program encompasses the following technical areas:

Rolled Sheet, Forgings, Extrusions, Castings, Fiber and Powder Metallurgy
Component Fabrication, Joining, Forming, Materials Removal
Fuels, Lubricants, Ceramics, Graphites, Non-Metallic Structural Materials
Solid State Devices, Passive Devices, Thermionic Devices

Your comments are solicited on the potential utilization of the information contained herein as applied to your present or future production programs. Suggestions concerning additional Manufacturing Methods development required on this or other subjects will be appreciated.

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ABSTRACT
VOLUME II - TECHNICAL DOCUMENTARY REPORT

ASD-TDR-62-1025
VOLUME II OF V

HIGH ENERGY FUELS PROJECT
THEORY OF DIBORANE PYROLYSIS

Analog computer evaluation of possible diborane pyrolysis mechanisms resulted in selection of one in which unstable species B_3H_7 and B_4H_8 play important roles. Rate constants were determined at 112.4°C. for the complex set of differential equations based on this mechanism to provide good agreement between computer-produced curves and those determined from extensive experimental data.

Diborane was pyrolyzed at 90.0, 100.0, 112.4, 126.1 and 140.0°C. for various periods of time, the system was quenched, and the products analyzed. A number of copyrolysis studies were also performed in which B_4H_{10}, B_5H_{11}, B_5H_9, $B_{10}H_{14}$, or H_2 was introduced initially, in order to study the effect of each of these species on the conversion of diborane and the formation of other species. After examination of the data, it was possible to postulate reaction mechanisms for diborane pyrolysis. Differential equations based on these mechanisms were derived, and rate constants at 112.4°C. were estimated. These equations were integrated with an analog computer, which produced curves corresponding to all components in the system. Rate constants were adjusted to achieve the best agreement possible between the experimental curves and those produced by the computer. Two series of copyrolysis studies corresponding to 2^3 and 2^4 factorial statistical patterns were then simulated on the computer. The curves were examined at a pyrolysis time of 90 minutes, and equations were derived of the form:

$$y = b_0 + b_1x_1 + b_2x_2 + b_{12}x_1x_2 + b_3x_3 + b_{13}x_1x_3 +$$
$$b_{23}x_2x_3 + b_{123}x_1x_2x_3 + \ldots + b_4x_4 + b_{14}x_1x_4 +$$
$$\ldots + b_{1234}x_1x_2x_3x_4$$

in which y is a response such as per cent of diborane converted, ratio of pentaborane to decaborane, etc., and the x terms are variables based on the partial pressure of B_4H_{10}, B_5H_{11}, etc., introduced initially. Sufficient data are available so that a 2^5 pattern may be calculated in which pyrolysis time may also be taken as a variable (x_5 = time).

* *

PUBLICATIONS REVIEW

This report has been reviewed and is approved.

FOR THE COMMANDER:

J H Marsh

JACK H. MARSH
Assistant Chief
Manufacturing Technology Laboratory
Directorate of Materials & Processes

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

THEORY OF DIBORANE PYROLYSIS

Introduction

In the pyrolysis of diborane, a series of higher and higher boranes is produced, with the ultimate products being hydrogen and a solid, non-volatile boron hydride polymer. In order to optimize the yield of any one of the intermediate boron hydrides, it was deemed necessary to make a thorough study of the diborane pyrolysis system both from experimental and theoretical approaches. A series of diborane pyrolysis studies was undertaken in the laboratory. The data obtained were then examined and analyzed by means of an analog computer.

This total report consists of five (5) volumes, viz.:

I. (U) Preliminary Design for a Large Scale Borane Plant

II. (U) Theory of Diborane Pyrolysis

III. (U) Process Development for Diborane Production

IV. (U) Process Development for Diborane Pyrolysis

V. (U) Process Development for Decaborane Alkylation

[redacted]

Results

Extensive screening both by hand and with an analog computer resulted in the selection of the diborane pyrolysis mechanism given in Table 1. The species B_3H_7 and B_4H_8 appear to be very important in the pyrolysis mechanism, although they cannot be observed directly. They may, however, be described by the following stationary state expressions:

$$B_3H_7 \propto \frac{(B_2H_6)^{1.5} + c_4(B_4H_{10})}{c_1\ (H_2) + (B_2H_6) + c_3(B_5H_9)}$$

$$B_4H_8 \propto \frac{(k_5-k_6)(B_5H_{11}) + 0.67k_3(B_4H_{10})}{(H_2) + c_2(B_2H_6)}$$

The set of differential equations appearing in Table 2, based on this mechanism, was utilized in computer studies to establish rate constants for 112.4°C. These constants were adjusted and refined to provide good agreement between computer-derived curves for the various pyrolysis products and those determined from the extensive laboratory data collected for the pyrolysis of diborane - alone and in the presence of other borane species. Intermediate and final values for these rate constants are compared in Table 3.

Typical applications of this information were illustrated in two series of copyrolysis studies simulated on the computer.

TABLE 1

Postulated Mechanism for Diborane Pyrolysis

$$B_2H_6 \rightleftharpoons 2BH_3 \qquad \text{rapid}$$

$$BH_3 + B_2H_6 \rightleftharpoons B_3H_9 \qquad \text{rapid}$$

$$B_3H_9 \rightleftharpoons B_3H_7 + H_2$$

$$B_3H_7 + B_2H_6 \longrightarrow B_5H_{11} + H_2$$

$$B_3H_7 + B_2H_6 \longrightarrow B_4H_{10} + BH_3$$

$$B_5H_{11} \longrightarrow B_4H_8 + BH_3$$

$$B_4H_8 + H_2 \rightleftharpoons B_4H_{10}$$

$$B_4H_8 + B_2H_6 \longrightarrow B_5H_{11} + BH_3$$

$$B_4H_{10} \longrightarrow B_3H_7 + BH_3$$

$$B_5H_{11} \longrightarrow B_5H_9 + H_2$$

$$B_5H_9 + B_3H_7 \longrightarrow B_8H_{14} + H_2$$

$$B_8H_{14} \longrightarrow B_8H_{12} + H_2 \qquad \text{rapid}$$

$$B_8H_{12} + B_2H_6 \longrightarrow B_{10}H_{16} + H_2 \qquad \text{rapid}$$

$$B_{10}H_{16} \longrightarrow B_{10}H_{14} + H_2 \qquad \text{rapid}$$

$$B_{10}H_{14} + BH_3 \longrightarrow B_{11}H_{15} + H_2$$

$$B_{11}H_{15} + B_2H_6 \longrightarrow B_{12}H_{12} + BH_3 + 3H_2 \qquad \text{rapid}$$

$$B_{12}H_{12} \longrightarrow \text{polymer}$$

TABLE 2

Differential Equations for Computer Studies

$$\frac{d(B_4H_{10})}{dt} = k_8(B_2H_6)\frac{(B_2H_6)^{1.5} + c_4(B_4H_{10})}{c_1(H_2) + (B_2H_6) + c_3(B_5H_9)}$$

$$+ (H_2)\frac{(k_5-2.36k_6)(B_5H_{11}) + 0.67k_3(B_4H_{10})}{(H_2) + c_2(B_2H_6)} - k_3(B_4H_{10})$$

$$\frac{d(B_5H_{11})}{dt} = k_1(B_2H_6)\frac{(B_2H_6)^{1.5} + c_4(B_4H_{10})}{c_1(H_2) + (B_2H_6) + c_3(B_5H_9)}$$

$$+ c_2(B_2H_6)\frac{(k_5-2.36k_6)(B_5H_{11}) + 0.67k_3(B_4H_{10})}{(H_2) + c_2(B_2H_6)} - k_5(B_5H_{11})$$

$$\frac{d(B_5H_9)}{dt} = k_6(B_5H_{11}) - k_7(B_5H_9)\frac{(B_2H_6)^{1.5} + c_4(B_4H_{10})}{c_1(H_2) + (B_2H_6) + c_3(B_5H_9)}$$

$$\frac{d(B_{10}H_{14})}{dt} = k_9(B_5H_9)\frac{(B_2H_6)^{1.5} + c_4(B_4H_{10})}{c_1(H_2) + (B_2H_6) + c_3(B_5H_9)} - k_{10}(B_{10}H_{14})(B_2H_6)^{0.5}$$

$$\frac{d(B_2H_6)}{dt} = 1.5k_4(H_2)\frac{(B_2H_6)^{1.5} + c_4(B_4H_{10})}{c_1(H_2) + (B_2H_6) + c_3(B_5H_9)}$$

$$- c_5(0.5k_8+k_1)(B_2H_6)\frac{(B_2H_6)^{1.5} + c_4(B_4H_{10})}{c_1(H_2) + (B_2H_6) + c_3(B_5H_9)}$$

$$- k_7(B_5H_9)\frac{(B_2H_6)^{1.5} + c_4(B_4H_{10})}{c_1(H_2) + (B_2H_6) + c_3(B_5H_9)}$$

$$- 1.5k_2(B_2H_6)^{1.5} - 0.5c_2(B_2H_6)\frac{(k_5-2.36k_6)(B_5H_{11}) + 0.67k_3(B_4H_{10})}{(H_2) + c_2(B_2H_6)}$$

$$+ 0.167k_3(B_4H_{10}) + 0.5(k_5-2.36k_6)(B_5H_{11}) - k_{10}(B_{10}H_{14})(B_2H_6)^{0.5}$$

TABLE 2 (Cont.)

Differential Equations for Computer Studies

$$\frac{d(H_2)}{dt} = -k_4(H_2)\frac{(B_2H_6)^{1.5} + c_4(B_4H_{10})}{c_1(H_2) + (B_2H_6) + c_3(B_5H_9)}$$

$$+ k_1(B_2H_6)\frac{(B_2H_6)^{1.5} + c_4(B_4H_{10})}{c_1(H_2) + (B_2H_6) + c_3(B_5H_9)}$$

$$+ 3.73k_9(B_5H_9)\frac{(B_2H_6)^{1.5} + c_4(B_4H_{10})}{c_1(H_2) + (B_2H_6) + c_3(B_5H_9)}$$

$$+ k_2(B_2H_6)^{1.5} - (H_2)\frac{(k_5-2.36k_6)(B_5H_{11}) + 0.67k_3(B_4H_{10})}{(H_2) + c_2(B_2H_6)}$$

$$+ 0.67k_3(B_4H_{10}) + k_6(B_5H_{11}) + 4k_{10}(B_{10}H_{14})(B_2H_6)^{0.5}$$

$$\frac{d(BH)_x}{dt} = k_{10}(B_{10}H_{14})(B_2H_6)^{0.5}$$

TABLE 3

Intermediate and Final Values for the Computer Study Rate Constants

112.4°C

	Intermediate	Final
k_1	1.06×10^{-4}	1.34×10^{-4}
k_2	1.34×10^{-4}	1.34×10^{-4}
k_3	2.45×10^{-1}	2.45×10^{-1}
k_4	1.44×10^{-4}	1.44×10^{-4}
k_5	2.17×10^{-1}	2.17×10^{-1}
k_6	1.40×10^{-2}	1.40×10^{-2}
k_7	3.44×10^{-4}	3.17×10^{-4}
k_8	3.75×10^{-5}	0
k_9	1.72×10^{-3}	1.58×10^{-3}
k_{10}	9.80×10^{-4}	9.80×10^{-4}
c_1	9.58×10^{-1}	9.58×10^{-1}
c_2	5.13×10^{-1}	5.13×10^{-1}
c_3	2.40×10	4.25
c_4	6.10×10^{2}	6.10×10^{2}
c_5	9.30×10^{-1}	1.00

Experimental Data

All of the laboratory data obtained are given in the Appendix, Tables I to XXV. Typical distribution patterns of the various borane species during a routine diborane pyrolysis are shown in Figures 1, 2 and 3.

Some of the runs were very fragmentary, having been made for some specific purpose. The pyrolysis of one atmosphere of diborane at 90.0°C (Table XI of the Appendix) was studied over the initial stages only for the purpose of determining the activation energy of the initial step in the pyrolysis. The pyrolysis of 0.5 atmosphere of diborane at 100.0°C (Table XV) was also part of the study of the initial reaction. Preparation of materials and much of the experimental procedure have been described elsewhere.[1,2] The equations derived from infrared reference spectra for B_4H_{10}, B_5H_9 and B_5H_{11} which were used to calculate the concentrations of these species in a 10 cm. infrared cell are:

(1) $P(B_4H_{10}) = 33.11D(4.65) - 1.38D(4.89) - 0.71D(5.53)$

(2) $P(B_5H_9) = 0.45D(4.65) - 6.49D(4.89) + 85.55D(5.53) - 0.16$

(3) $P(B_5H_{11}) = -3.90D(4.65) + 88.69D(4.89) - 1.18D(5.53) - 0.18$

In these equations, P is the partial pressure of the species indicated, and D is the difference in absorbance at the wavelength given (in microns) between the observed peak height and a base line drawn through the valley bottoms at 3.48 and 5.94 microns. These equations were derived some time after the pyrolysis work had begun, and not all of the values for the earliest runs were recalculated using these equations. For these runs, the values given for B_4H_{10}, B_5H_9 and B_5H_{11} were calculated using the equations of McCarty, et al(3). The McCarty equations give values which are believed to be fairly good, but they appear to have been designed primarily for mixtures in which B_5H_9 is the principal species, and they tend to give high values for B_5H_{11} when its concentration is high. The equations given above, which were determined in this laboratory, are felt to be more accurate for the types of mixtures encountered in the pyrolysis work, and most of the data have been analyzed using these equations.

After removal of the volatile hydrides from the bulb in which the pyrolysis had been performed, the decaborane was sublimed into the tubing connecting the bulb with the vacuum line. This section was then removed and weighed, the decaborane washed out and its weight determined by difference. The polymer remaining the bulb was then weighed, also by difference. The average volume of the pyrolysis bulbs was approximately 115 ml. The temperature at which the majority of the systems were most extensively studied was 112.4°C.

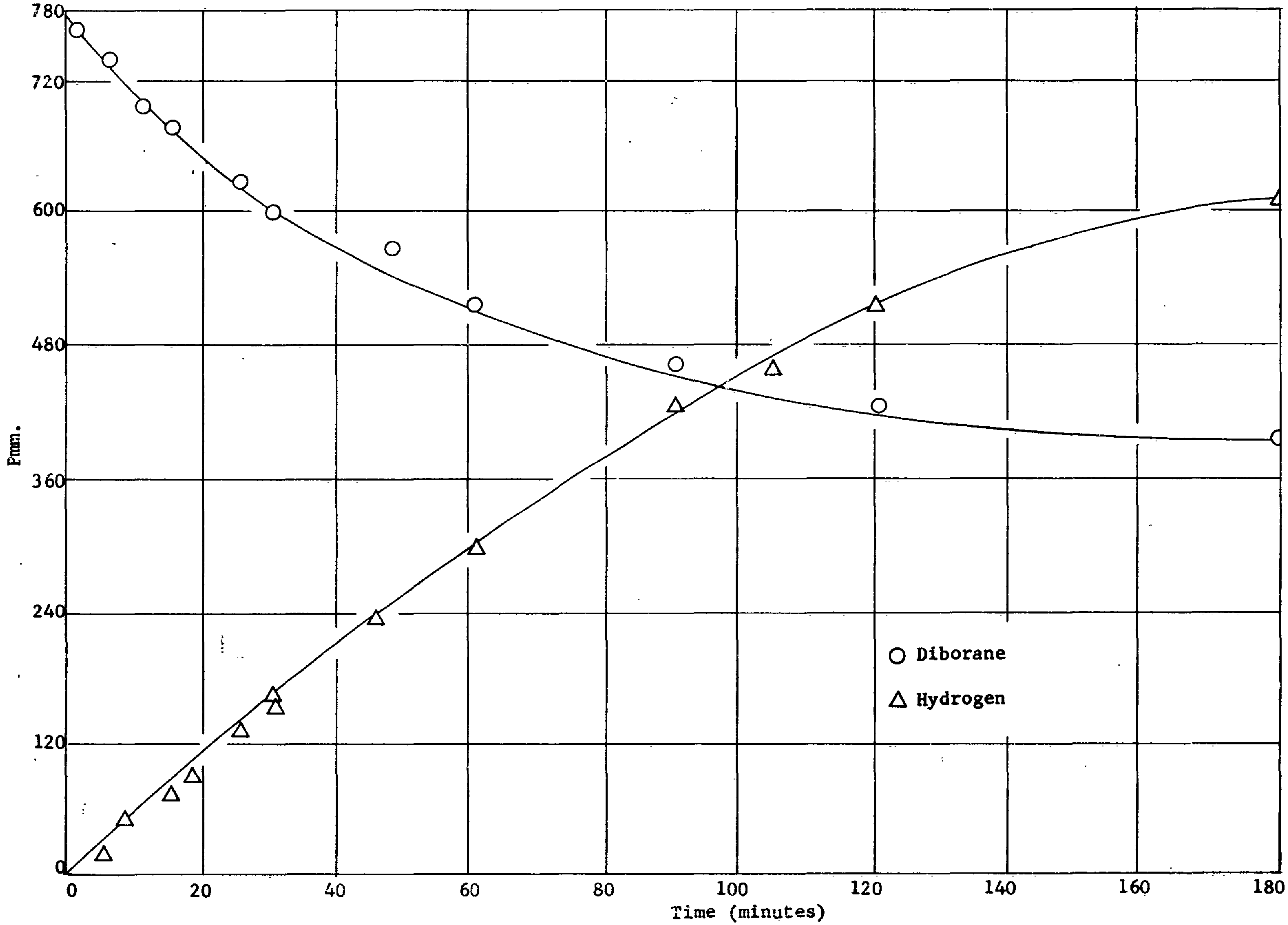

Figure 1. Disappearance of Diborane and Formation of Hydrogen in the Pyrolysis of Diborane at 112.4°C and an Initial Pressure of 760 mm.

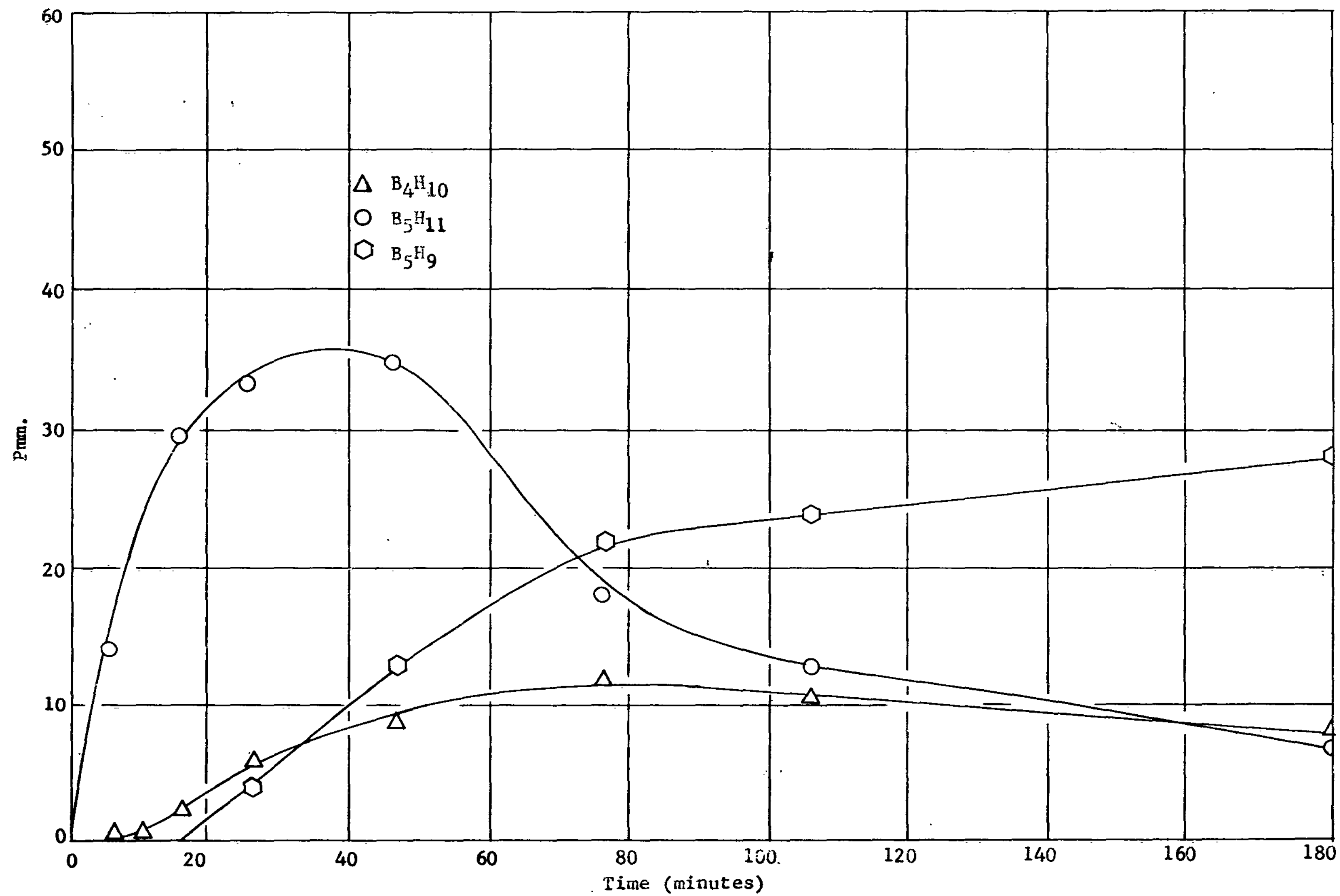

Figure 2. Formation of Tetraborane, Pentaborane, and Unstable Pentaborane by Pyrolysis of Diborane at 112.4°C and an Initial Pressure of 760 mm.

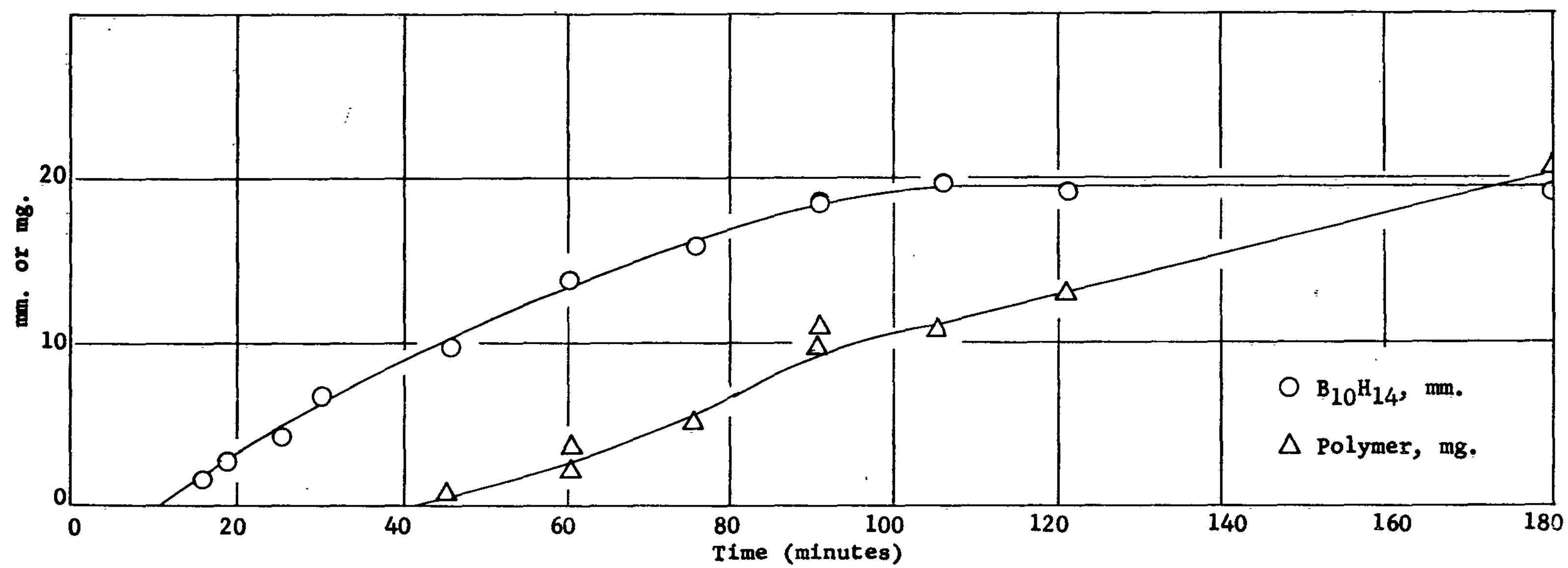

Figure 3. Rates of Formation of Decaborane and Non-Volatile Polymer

One experiment was performed in which diborane at one atmosphere initial pressure was pyrolyzed at 112.4°C and the hydrogen was periodically removed. This was done by using a bulb equipped with the five break-off tips and four seal-offs. The volatile contents of the bulb could then be removed, analyzed, and replaced in the bulb for further pyrolysis at 112.4°C. Analyses of the contents were made at cumulative pyrolysis times of 10, 20, 30, 45 and 60 minutes, with the hydrogen being removed and not replaced after each measurement. The $B_{10}H_{14}$ and $(BH)_x$ were measured at the end of the experiment. Data are given in Table XXIV of the Appendix. In this experiment, the B_5H_{11} built up to higher values than normally, whereas B_4H_{10} was considerably depressed.

In the copyrolysis of one atmosphere B_2H_6 and 125 mm. B_5H_9 at 112.4°C, the infrared spectrum indicated that an unidentified boron hydride formed which separated out with the intermediate fraction. Its pressure at run conditions was estimated by subtracting the total partial pressure of B_4H_{10}, B_5H_9 and B_5H_{11} (determined by infrared measurements) from the total pressure of the intermediate fraction. The data are given in Table XXV of the Appendix. Considerable scatter in the results is observed, but this is to be expected, since they were obtained by subtracting one large number from another, each of which may be in error by two per cent. A larger quantity of this compound was prepared, but it could not be characterized since the material is very unstable and is completely decomposed after a few minutes at room temperature. The compound has a strong infrared absorption peak at 6.3 microns. Principal decomposition products are B_2H_6, possibly some B_5H_9, a clear, non-volatile material, and a trace of hydrogen.

Pentaborane-9 and $B_{10}H_{14}$ by themselves appear to be stable at the temperatures studied. In one experiment, 10 mg. of $B_{10}H_{14}$ was pyrolyzed at 112.4°C for 35 minutes. In another run, 25 mm. of B_5H_9 was pyrolyzed at 112.4°C for 60 minutes. In each case the compound was recovered quantitatively at the end of the experiment.

The gas phase equilibrium reaction

$$(4) \qquad 2B_5H_{11} + 2H_2 \rightleftharpoons 2B_4H_{10} + B_2H_6$$

was studied extensively. This equilibrium appears to hold in the later stages of pyrolysis when sufficient quantities of all species involved are present. Calculations were made on the pyrolysis of diborane alone and on several of the copyrolysis systems. Data are given in Table 4. From a plot of ln K_p versus $1/T$, the enthalpy and entropy changes for the reaction were determined as -7.56 kcal./mole and -19.5 e.u./mole.

TABLE 4

Equilibrium Constants for the Reaction

$2B_5H_{11(g)} + 2H_{2(g)} = 2B_4H_{10(g)} + B_2H_{6(g)}$

Temp. (°C)	Reactants	K_p (atm.$^{-1}$)
100.0	B_2H_6 760 mm.	1.52
	B_2H_6 760 mm., B_4H_{10} 50 mm.	1.50
	B_5H_{11} 60 mm., H_2 250 mm.	1.37
		Ave. 1.46
112.4	B_2H_6 760 mm.	1.06
	B_2H_6 760 mm., B_4H_{10} 50 mm.	1.02
	B_2H_6 760 mm., B_5H_{11} 50 mm.	0.99
	B_2H_6 760 mm., B_5H_9 125 mm.	1.01
	B_5H_{11} 50 mm., H_2 500 mm.	1.03
		Ave. 1.02
126.1	B_2H_6 760 mm.	0.77
140.0	B_2H_6 760 mm.	0.54

The initial rate of diborane decomposition was also studied. At this stage the principal over-all reaction is

(5) $$5B_2H_6 \longrightarrow 2B_5H_{11} + 4H_2$$

Comparison of the rates of initial pressures of 1.0 and 0.5 am. B_2H_6 indicated that the initial reaction is 1.5 order in B_2H_6. The rate constants obtained are given in Table 5. The activation energy for the reaction was determined as 22.1 kcal./mole and the pre-exponential factor as 9.6×10^{10}.

TABLE 5

The 1.5 Order Rate Constants in the Initial Decomposition of B_2H_6

Temp. (°C)	$k_{1.5}$ (mm.$^{-0.5}$min.$^{-1}$)	$k_{1.5}$ (cc.$^{0.5}$mole$^{-0.5}$sec.$^{-1}$)
126.1	9.33×10^{-4}	7.76×10^{-2}
112.4	3.34×10^{-4}	2.72×10^{-2}
100.0	1.27×10^{-4}	1.02×10^{-2}
90.0	6.34×10^{-5}	5.03×10^{-3}

Computer and Statistical Studies

The pyrolysis data described in the preceding section have proved to be of value in providing a qualitative understanding of the interactions involved in diborane pyrolysis. A limited amount of quantitative data have also been derived from this study, specifically the kinetic constants of the initial reaction and thermodynamics of the B_5H_{11}-H_2-B_2H_6-B_4H_{10} equilibrium reaction. In order to derive the maximum value from the information gathered in the kinetic studies, it was necessary to correlate all of the data in a single, comprehensive pyrolysis scheme. This was done by postulating a number of reasonable pyrolysis mechanisms and deriving rate equations therefrom.

Because the interactions that take place during the pyrolysis of diborane are complex, the rate equations were non-integrable. For this reason an analog computer was utilized to integrate the differential equations and produce curves corresponding to each of the major species as a function of time during pyrolysis.

A number of simple mechanisms for individual species were examined by hand for qualitative agreement with observed data. This was done by estimating rate constants from the rate equations, using the slopes of the experimental curves to ascertain whether the values of the rate constants were positive or negative. Any mechanisms requiring negative rate constants were discarded. For the mechanisms deemed possible, the rate of formation or disappearance of the species involved was calculated at some pyrolysis time other than those times used to estimate the rate constants. By comparison with the observed rate, some mechanisms were deemed more likely than others. Data obtained for pyrolysis studies at 112.4°C were used since the most extensive work was done at this temperature. The most likely mechanisms were then set up on the computer for further screening. On the computer the rate constants were adjusted to give the best possible agreement between the experimental curves and the curves produced by the computer.

This initial work gave rough values for 112.4°C rate constants and indicated what modifications of the equations would be necessary to refine the system. The final set of equations examined is given in Table 2. The rate constant values obtained are given in Table 3. Two sets of constants are given. The set labeled "intermediate" was used for the statistical studies based on a 2^4 pattern (see below). Upon completion of this study, additional computer time was available, and final adjustments were made on the constants to give the set labeled "final". This set represents the best agreement between computer and experimental curves to the present time, and was used for a statistical study based on a smaller 2^3 pattern. Although the intermediate constant values do not represent as accurate a description of the pyrolysis system as the final values do, it is felt that the 2^4 factorial pattern will still give a measure of species interactions and will describe the effects of one species on the relative yield of another.

The mechanism of B_2H_6 pyrolysis from which the rate equations in Table 2 were derived is given in Table 1. The species B_3H_7 and B_4H_8 appear to be very important in the pyrolysis mechanism, although they cannot be observed directly. They may, however, be described by the following stationary state expressions which were used in deriving the differential equations in Table 2:

$$B_3H_7 \propto \frac{(B_2H_6)^{1.5} + c_4(B_4H_{10})}{c_1(H_2) + (B_2H_6) + c_3(B_5H_9)} \tag{6}$$

$$B_4H_8 \propto \frac{(K_5 - k_6)(B_5H_{11}) + 0.67k_3(B_4H_{10})}{(H_2) + c_2(B_2H_6)} \tag{7}$$

The equations in Table 2 describe reasonably well the boron hydride pyrolysis systems determined experimentally except for the following principal discrepancies: (1) The computer curve for $B_{10}H_{14}$ is low in the B_2H_6—B_4H_{10} and B_2H_6—B_5H_{11} copyrolysis systems but high in the B_5H_9-B_2H_6 copyrolysis system. Introduction of a term describing the formation of $B_{10}H_{14}$ from B_5H_{11}, B_4H_{10} or B_4H_8, together with a reduction in the value for k_9, would probably correct these discrepancies. The apparent necessity for this term is also indicated from the need to change the term (k_5-k_6) to $(k_5-2.36k_6)$ in the stationary state expression for B_4H_8 during computer analysis; (2) The computer curve for B_5H_{11} is high in the initial portion of the B_5H_{11}—B_2H_6 copyrolysis system but is low in the systems in which B_2H_6 starts at 0.5 atm. (with and without additional H_2 present initially); (3) The B_4H_{10} curve is low in the 0.5 atm. B_2H_6-0.5 atm. H_2 system, probably due to the low B_5H_{11} curve.

The equations in Table 2 simulate reasonably well the gross characteristics of diborane pyrolysis and the several copyrolysis systems studied. One could, therefore, utilize the computer to simulate diborane pyrolysis over a fairly wide range of conditions of diborane pressure, addition of hydrogen to the diborane stream and recycle of intermediates. The curves produced could be expected to reasonably well reproduce those which would be obtained in the laboratory, should the experiments be done.

The output of the computer is in the form of curves, as has been previously stated. While the computer allows very rapid evaluation of proposed system changes, each change in conditions requires a separate run on the computer. Since the curves do not provide ready extrapolation to a different set of conditions without actually making a run on the computer, a means was sought for making such an extrapolation possible.

Such a means was found in the application of statistical design to computer studies. A set of experiments was planned to fit a 2^4 factorial design to determine the main effects and interactions of four variables at two levels each. The variables were chosen to simulate various conditions of recycle.

For statistical calculations, reference was made to the Box Method of experimental planning.[4,5] The 2^4 factorial pattern required making a series of runs on the computer beginning with 1 atm. B_2H_6 and various amounts of H_2, B_4H_{10}, B_5H_9 and B_5H_{11} introduced initially. The experiments and starting conditions are given in Table 6. The curves were examined at 90 minutes pyrolysis time, and equations of the form

$$(8)\quad y = b_0 + b_1x_1 + b_2x_2 + b_{12}x_1x_2 + b_3x_3 + b_{13}x_1x_3 + b_{23}x_2x_3 + b_{123}x_1x_2x_3 + b_4x_4 + b_{14}x_1x_4 + b_{24}x_2x_4 + b_{124}x_1x_2x_4 + b_{34}x_3x_4 + b_{134}x_1x_3x_4 + b_{234}x_2x_3x_4 + b_{1234}x_1x_2x_3x_4$$

were derived, in which y is a response such as percentage of B_2H_6 converted, ratio of B_5H_9 to $B_{10}H_{14}$, etc. The constant coefficients b_i provide a measure of the effect of x_i on the response. The various quantities for y and the corresponding values obtained for the b_i terms are given in Table 7. The x terms are the independent variables based on the pressure of the various species added initially and are described by the coding equations:

$$(9)\quad x_1 = \frac{P(H_2) - 190}{190}$$

$$(10)\quad x_2 = \frac{P(B_4H_{10}) - 12.5}{12.5}$$

$$(11)\quad x_3 = \frac{P(B_5H_{11}) - 12.5}{12.5}$$

$$(12)\quad x_4 = \frac{P(B_5H_9) - 12.5}{12.5}$$

in which the P terms are the initial pressures in mm. of the species indicated. Equation (8) gives the value of a given response after 90 minutes of pyrolysis at 112.4°C as a function of the materials initially present along with one atmosphere of diborane. The terms such as $b_{ij}x_ix_j$, etc. describe the effect of the interaction of species i and j on the

TABLE 6

Starting Conditions Employed in Obtaining Computer Curves for the 2^4 Factorial Design[a]

Exp. No.	Initial Species (mm.)			
	H_2	B_4H_{10}	B_5H_{11}	B_5H_9
1	0	0	0	0
2	380	0	0	0
3	0	25	0	0
4	380	25	0	0
5	0	0	25	0
6	380	0	25	0
7	0	25	25	0
8	380	25	25	0
9	0	0	0	25
10	380	0	0	25
11	0	25	0	25
12	380	25	0	25
13	0	0	25	25
14	380	0	25	25
15	0	25	25	25
16	380	25	25	25
17[b]	190	12.5	12.5	12.5

(a) All runs contained one atm. B_2H_6 initially in addition to the species indicated.
(b) Center point of pattern.

TABLE 7

Responses and Constant Values
Obtained in the 2^4 Factorial Design[a]

y	% B_2H_6 Converted[b]	% B_5H_9 Yield[c]	$\frac{(B_5H_9)}{(B_{10}H_{14})}$[d]	$\frac{(B_{10}H_{14})\ \text{Present}}{(B_{10}H_{14})\ \text{Converted}}$[e]
b_0	+30.75	+13.18	+0.820	+0.771
b_1	-4.98	-0.61	-0.038	-0.018
b_2	-4.11	+1.50	+0.023	-0.033
b_{12}	-0.10	-0.05	-0.013	+0.005
b_3	-0.34	+2.20	+0.041	-0.053
b_{13}	-0.07	+0.01	-0.015	-0.005
b_{23}	0.00	+0.03	-0.001	+0.023
b_{123}	-0.02	+0.04	+0.003	-0.002
b_4	+1.30	-7.73	-0.560	-0.153
b_{14}	+0.96	-1.10	-0.059	-0.005
b_{24}	+0.03	-0.25	+0.028	+0.015
b_{124}	-0.08	-0.13	+0.004	-0.011
b_{34}	0.00	-0.06	+0.049	+0.046
b_{134}	-0.08	-0.20	+0.004	0.000
b_{234}	+0.02	0.00	-0.005	-0.017
b_{1234}	-0.03	0.00	-0.002	+0.003

(a) Calculated from data at 90 min. pyrolysis time.
(b) Per cent of B_2H_6 initially present which has decomposed.
(c) Based on B_5H_9 over and above that present initially divided by the B_5H_9 which would be formed if all decomposed B_2H_6 formed B_5H_9.
(d) B_5H_9 over and above that present initially divided by the $B_{10}H_{14}$ present.
(e) $B_{10}H_{14}$ converted determined from computer curve representing $(BH)_x$.

system beyond the individual effects of i and j alone. Sufficient data are available that a 2^5 pattern could be calculated, in which pyrolysis time may also be employed as a variable. For instance, the responses obtained from the curves at 60 and 90 minutes may be used to set up the 2^5 pattern. No further computer work would be necessary for such a calculation.

A 2^3 pattern, obtained after final adjustment of the rate constants on the computer, was calculated similarly. Variables studied were (1) initial pressure of B_2H_6, (2) initial pressure of B_4H_{10}, and (3) initial pressure of a mixture composed of 50 per cent B_5H_{11} and 50 per cent B_5H_9. The experiments and starting conditions are given in Table 8. The curves were examined at 90 minutes pyrolysis time, and equations of the form

$$(13) \qquad y = b_0 + b_1x_1 + b_2x_2 + b_{12}x_1x_2 + b_3x_3 + b_{13}x_1x_3 + b_{23}x_2x_3 + b_{123}x_1x_2x_3$$

were derived in which the y and b terms are of the same type as those described for the 2^4 design. The x variables are described by the coding equations:

$$(14) \qquad x = \frac{P(B_2H_6) - 605}{155}$$

$$(15) \qquad x_2 = \frac{P(B_4H_{10}) - 7.5}{7.5}$$

$$(16) \qquad x_3 = \frac{P(B_5H_{11} + B_5H_9) - 12.5}{12.5}$$

in which P is the initial pressure in mm. of the species indicated. The responses investigated and the corresponding values for the b terms are given in Table 9.

The trends in response values as predicted by Equations (8) and (13) were verified by comparison with the trends observed in response values calculated from the experimental data. In general, the predicted trends agreed with the observed ones. One major discrepancy, however, was observed. The 2^4 factorial equation for $y = (B_5H_9)/(B_{10}H_{14})$ predicts a higher value for this response when hydrogen is added initially <u>except</u> if B_5H_9 is present initially, when a lower response value is predicted. However, experiment indicates that hydrogen present initially increases the value for the B_5H_9 to $B_{10}H_{14}$ ratio whether B_5H_9 is present initially or not. Some adjustment of the differential equations (Table 2) may be indicated in order to reduce B_5H_9 decomposition when hydrogen is initially present. This may possibly be accomplished by reducing the concentration of B_3H_7 under these conditions by: (1) increasing the fraction of B_4H_{10} decomposition to B_4H_8 and H_2 and thus reducing the value for c_4 (Table 3), or (2) increasing the reactivity of B_3H_7 with hydrogen by increasing the values for k_4 and c_1.

TABLE 8

Starting Conditions Employed in Obtaining Computer Curves for the 2^3 Factorial Design

Exp. No.	Initial Species (mm.)		
	B_2H_6	B_4H_{10}	$B_4H_{11} + B_5H_9$ (a)
1	450	0	0
2	760	0	0
3	450	15	0
4	760	15	0
5	450	0	25
6	760	0	25
7	450	15	25
8	760	15	25
9 (b)	605	7.5	12.5

(a) All mixtures composed of 50% B_5H_{11} and 50% B_5H_9.
(b) Center point of pattern.

TABLE 9

Responses and Constant Values Obtained in the 2^3 Factorial Design (a)

y (b)	% B_2H_6 Converted	% B_5H_9 Yield	$\frac{(B_5H_9)}{(B_{10}H_{14})}$	$\frac{(B_{10}H_{14})}{(B_{10}H_{14})\ Conv.}$
b_0	+33.45	+17.91	+0.822	+1.075
b_1	+2.32	-0.82	+0.014	-0.149
b_2	-0.37	+1.38	-0.006	-0.031
b_{12}	+0.07	-0.48	+0.005	+0.007
b_3	-0.73	-3.04	-0.333	-0.231
b_{13}	+0.04	+0.50	+0.061	+0.053
b_{23}	-0.07	+0.05	+0.026	+0.014
b_{123}	+0.04	-0.01	-0.010	0.000

(a) Calculated from data at 90 min. pyrolysis time.
(b) For description of response terms, see Table XXXII.

Inspection of the values in Tables 7 and 9 will provide information regarding the relative importance of the various terms in Equations (8) and (13). In Table 7, for example, the large positive value of coefficient b_3 in the column for "per cent B_5H_9 yield" indicates that recycle of B_5H_{11} to the reactor will increase the yield of B_5H_9. The value of b_2 indicates that recycle of tetraborane would also be favorable. The negative value of b_4 indicates that recycled B_5H_9 would disappear by further reaction more rapidly than fresh B_5H_9 would be formed, as would be expected. The majority of the interaction terms in all of these systems are fairly small, as is also expected.

The equations may be used to predict responses by substitution of the appropriate coding equations and coefficients. For example, suppose that it is desired to determine the effect of recycle of intermediates on the ratio of B_5H_9 to $B_{10}H_{14}$ after 90 minutes pyrolysis at 112.4°C. Equations (9), (10), (11) and (12) are substituted into Equation (8). The appropriate values for the coefficients b_i are then substituted from Table 7. The result is an equation giving the ratio $(B_5H_9)/(B_{10}H_{14})$ as a function of the partial pressures of H_2, B_4H_{10}, B_5H_{11} and B_5H_9 in one atmosphere of diborane at the beginning of pyrolysis. Substitution of the desired values for the pressures of these species will give a numerical value for the $(B_5H_9)/(B_{10}H_{14})$ ratio after 90 minutes of pyrolysis at 112.4°C.

A similar set of equations could be derived for any other pyrolysis times, or time of pyrolysis could be included as a variable in a more extensive equation. The computer data already gathered would be sufficient for either procedure.

Insufficient time was available to investigate the effect of temperature on the system. This would require some further refinement of the rate equations and adjustment of the rate constants to give curves corresponding to those obtained experimentally at other temperatures.

Conclusions and Recommendations

1. A series of chemical equations has been developed which describes the mechanism of diborane pyrolysis. This mechanism was selected on the basis of close agreement between analog computer calculations and extensive pyrolysis data accumulated in the laboratory.

2. The unstable borane species B_3H_7 and B_4H_8 are important intermediates in the chain of pyrolysis reactions.

3. Assigned 112.4°C rate constants for the set of differential equations corresponding to the selected pyrolysis mechanism provide a means of simulating and evaluating various pyrolysis situations at this temperature.

4. A statistical design pattern (Box Method) enables the ready extrapolation of computer results to a different set of conditions without actually making a run on the computer. Sufficient data are available to permit calculation of a 2^5 statistical pattern.

5. The effect of temperature on the system should be investigated and defined. This can be accomplished by the refinement of the rate equations and adjustment of rate constants to give computer curves corresponding to those obtained experimentally at other temperatures.

6. The body of information thus obtained should be used to evaluate practical pyrolysis systems and guide process development programs for the manufacture of the higher boranes.

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A P P E N D I X

Diborane Pyrolysis Studies - Experimental Data

APPENDIX

LIST OF TABLES

Tables I - XXV
Pressure of Major Species in Pyrolysis Systems

LIST OF TABLES (Cont.)

TABLE I

Pressure of Major Species in Pyrolysis of 1 Atm. B_2H_6 at 112.4°C

Species	Time (min.)																		
	5.0	7.5	9.0	10.0	12.5	15.0	18.0	25.0	30.0	35.0	45.0	60.0	75.0	90.0	105.0	120.0	140.0	160.0	180.0
H_2 (mm.)	25	40	52	50	64	80	90	132	159	185	222	301		415	460	504	541	591	609
B_2H_6 (mm.)	730	717	692	690	679	672	642	622	594	580	567	513	499	459	439	423	413	395	392
B_4H_{10} (mm.)	1.4	2.0		2.2	2.7	3.6		7.0		8.6	8.8	11.2	10.4	10.0	9.4	9.3	8.0	7.9	6.9
B_5H_9 (mm.)	0.3	0.5		0.8	1.3	2.4		6.1		9.3	12.2	16.2	17.8	19.9	20.6	22.8	22.5	25.3	24.7
B_5H_{11} (mm.)	11.0	16.0		17.2	22.7	24.6		29.8		30.1	26.4	22.6	17.8	14.0	11.6	10.6	7.7	7.0	5.9
$B_{10}H_{14}$ (mm.)	-	-	-	-	-	0.9	2.0	3.9	5.2	6.8	9.2	13.9	15.5	18.3	19.4	19.2	19.6	19.1	19.2
$B_{10}H_{14}$ (mg.)	-	-	-		-	0.5	1.2	2.3	3.1	4.0	5.5	8.3	9.1	11.0	11.6	11.4	11.6	11.3	11.2
$(BH)_x$ (mg.)	-	-	-		-	-	-	-	-	2.4	0.5	2.8	4.8	9.7	10.2	12.8	16.8	20.6	20.5

TABLE II

Pressure of Major Species in Pyrolysis of 0.5 Atm. B_2H_6 at 112.4°C

Species	Time (min.)										
	5.0	7.5	10.0	12.5	15.0	30.0	60.0	90.0	120.0	150.0	180.0
H_2 (mm.)	9.6	14.8	18.8	23.5	27.6	58.1	117	170	213	247	274
B_2H_6 (mm.)	366	363	355	355	348	322	284	256	234	213	201
B_4H_{10} (mm.)	0.4	0.5	0.6	0.8	0.9	3.0	4.2	4.6	4.5	4.2	3.8
B_5H_9 (mm.)	-	-	-	0.2	0.6	3.6	7.4	10.2	11.9	12.8	13.7
B_5H_{11} (mm.)	4.1	6.5	7.8	9.0	10.3	16.3	14.9	11.6	8.7	6.7	5.4
$B_{10}H_{14}$ (mm.)	-	-	-	-	-	2.0	5.0	7.6	9.2	9.6	9.6
$B_{10}H_{14}$ (mg.)	-	-	-	-	-	1.1	3.0	4.4	5.2	5.4	5.5
$(BH)_x$ (mg.)	-	-	-	-	-	trace	trace	3.7	4.3	6.2	7.9

TABLE III

Pressure of Major Species in Copyrolysis of 0.5 Atm. B_2H_6 and 0.5 Atm. H_2 at 112.4°C

Species	Time (min.)					
	30.0	60.0	90.0	120.0	150.0	180.0
H_2 (mm.)	420	444	468	487	508	520
B_2H_6 (mm.)	343	322	311	301	291	276
B_4H_{10} (mm.)	6.8	7.7	7.3	6.8	6.3	5.5
B_5H_9 (mm.)	1.9	4.7	6.5	8.9	10.2	11.1
B_5H_{11} (mm.)	8.5	8.8	7.8	6.8	6.2	5.4
$B_{10}H_{14}$ (mm.)	0.7	1.7	3.4	3.7	5.2	5.7
$B_{10}H_{14}$ (mg.)	0.4	1.0	2.0	2.1	3.0	3.4
$(BH)_x$ (mg.)	-	0.8	0.8	1.2	2.3	2.4

TABLE IV

Pressure of Major Species in Copyrolysis of 760 mm. B_2H_6 and 50 mm. B_4H_{10} at 112.4°C

Species	Time (min.) 10.0	20.0	30.0	45.0
H_2 (mm.)	110	178	244	329
B_2H_6 (mm.)	681	640	602	565
B_4H_{10} (mm.)	7.4	10.0	11.6	12.2
B_5H_9 (mm.)	5.8	11.3	15.3	19.2
B_5H_{11} (mm.)	44.7	38.2	32.1	24.5
$B_{10}H_{14}$ (mm.)	3.9	9.3	13.3	18.3
$B_{10}H_{14}$ (mg.)	2.3	5.4	7.9	11.0
$(BH)_x$ (mg.)	1.0[a]	0.8	3.9	6.4

(a) May contain boric oxide.

TABLE V

Pressure of Major Species in Copyrolysis of 1 Atm. B_2H_6 and 50 mm. B_5H_{11} at 112.4°C

Species	Time (min.)			
	15.0	30.0	45.0	60.0
H_2 (mm.)	103	205	297	379
B_2H_6 (mm.)	684	612	577	544
B_4H_{10} (mm.)	6.7	10.1	11.7	12.2
B_5H_9 (mm.)	9.2	18.1	20.0	23.9
B_5H_{11} (mm.)	43.1	33.5	26.2	21.0
$B_{10}H_{14}$ (mm.)	8.2[a]	14.8	18.7	21.6
$B_{10}H_{14}$ (mg.)	4.9[a]	8.6	11.0	12.8
$(BH)_x$ (mg.)	1.4[a]	3.8	7.0	12.2

(a) May include glass chips.

TABLE VI

Pressure of Major Species in Copyrolysis of 1 Atm. B_2H_6 and 25 mm. B_5H_9 at 112.4°C

Species	Time (min.)							
	5.0	10.0	20.0	30.0	40.0	45.0	50.0	60.0
H_2 (mm.)	32	68	135	195	254	277	307	351
B_2H_6 (mm.)	715	701	654	611	575	558	544	524
B_4H_{10} (mm.)	1.7	2.5	5.3	7.7	9.3	9.8[a]	10.3	10.5
B_5H_9 (mm.)	23.4	21.5	21.4	22.2	24.0	22.8[a]	25.0	25.2
B_5H_{11} (mm.)	10.5	17.2	24.3	24.4	23.6	22.5[a]	21.4	18.0
$B_{10}H_{14}$ (mm.)	1.7	3.8	8.2	12.0	16.0	16.2	17.5	19.0
$B_{10}H_{14}$ (mg.)	1.0	2.2	4.8	7.2	9.2	9.7	10.5	11.4
$(BH)_x$ (mg.)	-	0.7	1.8	2.6	3.5	4.8	6.0	7.8

(a) Spectrophotometer was not operating at maximum accuracy.

TABLE VII

Pressure of Major Species in Copyrolysis of 1 Atm. B_2H_6 and 125 mm. B_5H_9 at 112.4°C

Species	Time (min.)									
	3.0	5.0	10.0	15.0	20.0	30.0	40.0	50.0	60.0	90.0
H_2 (mm.)	30	51	107	158	199	283	363	423	482	612
B_2H_6 (mm.)	712	705	684	656	624	583	553	509	489	432
B_4H_{10} (mm.)	1.4	1.4	2.0	2.2	3.3	4.9	5.0	6.0	6.1	6.6
B_5H_9 (mm.)	107	105	106	100	97	94	89	89	88	80
B_5H_{11} (mm.)	4.5	4.6	6.8	8.0	9.0	9.0	8.8	8.3	8.3	6.1
$B_{10}H_{14}$ (mm.)	2.5	5.8	12.3	16.4	19.9	23.4	24.9	24.1	24.8	25.8
$B_{10}H_{14}$ (mg.)	1.5	3.4	7.1	9.8	11.9	13.6	14.7	13.9	14.6	15.3
$(BH)_x$ (mg.)	0.2	1.2	1.9	3.0	4.8	9.0	15.4	18.3	22.7	31.4

TABLE VIII

Pressure of Major Species in Copyrolysis of 1 Atm. B_2H_6 and 10 mg. $B_{10}H_{14}$ at 112.4°C

Species	Time (min.)				
	5.0	10.0	25.0	35.0	60.0
H_2 (mm.)	42	78	162	218	328
B_2H_6 (mm.)	728	693	620	582	518
B_4H_{10} (mm.)	1.5	2.9	7.5	9.5	11.4
B_5H_9 (mm.)	0.0	1.2	5.6	9.0	15.3
B_5H_{11} (mm.)	10.5	18.8	28.4	27.9	21.0
$B_{10}H_{14}$ (mm.)	10.4	8.8	9.2	11.2	16.5
$B_{10}H_{14}$ (mg.)	6.2	5.2	5.5	6.7	9.7
$(BH)_x$ (mg.)	3.6	6.6	12.1	10.5	11.7

TABLE IX

Pressure of Major Species in Copyrolysis of 50.0 mm. B_5H_{11} and 500 mm. H_2 at 112.4°C

Species	Time (min.)						
	3.0	5.0	10.0	18.0	30.0	45.0	10.0[a]
H_2 (mm.)	486	488	475	471	481	471	30.9
B_2H_6 (mm.)	23.5	53.2[b]	55.9	72.7	87.1	92.2	33.1[b]
B_4H_{10} (mm.)	32.2	32.4[b]	17.9	10.0	5.2	2.6	5.0[b]
B_5H_9 (mm.)	0.6	-[b]	2.1	2.9	3.5	3.5	4.7[b]
B_5H_{11} (mm.)	13.3	9.2[b]	9.3	5.5	2.7	1.5	11.0[b]
$B_{10}H_{14}$ (mm.)	0.2	0.3	0.7	1.2	1.5	1.7	5.5
$B_{10}H_{14}$ (mg.)	0.1	0.2	0.4	0.7	0.9	1.0	3.3
$(BH)_x$ (mg.)	-	-	-	-	-	-	2.6

(a) No hydrogen present initially.
(b) Values not considered accurate.

TABLE X

Pressure of Major Species in Copyrolysis of 1 Atm. B_2H_6, 400 mm. H_2 and 25 mm. B_5H_9 at 112.4°C

Species	Time (min.)	
	45.0	90.0
H_2 (mm.)	598	732
B_2H_6 (mm.)	613	550
B_4H_{10}[a] (mm.)	15.6	13.2
B_5H_9[a] (mm.)	28.5	31.9
B_5H_{11}[a] (mm.)	15.7	10.5
$B_{10}H_{14}$ (mm.)	10.1	17.5
$B_{10}H_{14}$ (mg.)	6.0	10.4
$(BH)_x$ (mg.)	2.8	7.2

(a) Calculated using equations of McCarty, et al.[3]

TABLE XI

Pressure of Major Species in
Pyrolysis of 1 Atm. B_2H_6 at 90.0°C

Species	Time (min.) 10.0	15.0	20.0	25.0
H_2 (mm.)	10.6	16.1	20.0	23.6
B_2H_6 (mm.)	749	740	734	725
B_4H_{10}[(a)] (mm.)	1.5	1.2	1.0	0.9
B_5H_{11}[(a)] (mm.)	4.6	7.6	9.1	11.3

(a) Calculated using equations of McCarty, et al.[(3)]

TABLE XII

Pressure of Major Species in
Pyrolysis of 50 mm. B_5H_{11} at 90.0°C

Species	Time (min.)				
	3.0	6.0	10.0	15.0	20.0
H_2 (mm.)	2.3	4.7	7.4	10.2	13.3
B_2H_6 (mm.)	5.8	9.6	13.0	15.7	18.4
B_4H_{10} (mm.)	1.2	2.1	2.8	3.1	3.7
B_5H_9 (mm.)	0.2	0.6	1.0	1.7	1.9
B_5H_{11} (mm.)	41.5	35.8	31.0	26.6	23.2
$B_{10}H_{14}$ (mm.)	1.1	2.1	2.6	3.4	3.8
$B_{10}H_{14}$ (mg.)	0.7	1.3	1.6	2.1	2.4
$(BH)_x$ (mg.)	-	-	0.8	1.3	1.9

TABLE XIII

Pressure of Major Species in
Pyrolysis of 74 mm. B_4H_{10} at 90.0°C

Species	Time (min.)		
	5.0	10.0	15.0
H_2 (mm.)	37.1	53.2	61.3
B_2H_6 (mm.)	5.5	8.8	11.8
B_4H_{10} (mm.)	35.4	24.7	19.8
B_5H_9 (mm.)	0.5	1.1	1.9
B_5H_{11} (mm.)	14.5	16.8	17.4
$B_{10}H_{14}$ (mm.)	3.0	3.8	4.6
$B_{10}H_{14}$ (mg.)	1.9	2.4	2.9
$(BH)_x$ (mg.)	0.9	1.0	1.2

TABLE XIV

Pressure of Major Species in Pyrolysis of 1 Atm. B_2H_6 at 100.0°C

Species	Time (min.)							
	5.0	10.0	12.5	15.0	90.0	120.0	150.0	180.0
H_2 (mm.)	10.0	19.9	24.7	28.9	163	217	266	318
B_2H_6 (mm.)	746	729	724	722	602	578	550	522
B_4H_{10} (mm.)	1.4[a]	1.1[a]	0.8[a]	0.9[a]	9.1	11.1	11.6	12.2
B_5H_9 (mm.)	-	-	-	-	7.0	9.9	11.7	13.5
B_5H_{11} (mm.)	8.2[a]	13.2[a]	14.9[a]	16.6[a]	30.6	28.0	22.8	19.4
$B_{10}H_{14}$ (mm.)	-	-	-	-	6.3	9.8	12.7	13.7
$B_{10}H_{14}$ (mg.)	-	-	-	-	3.9	5.9	7.7	8.4
$(BH)_x$ (mg.)	-	-	-	-	1.5	2.2	4.4	7.2

(a) Calculated using equations of McCarty, et al.[3]

TABLE XV

Pressure of Major Species in
Pyrolysis of 0.5 Atm. B_2H_6 at 100.0°C

Species	Time (min.)					
	5.0	7.5	10.0	12.5	15.0	17.5
H_2 (mm.)	4.3	6.1	7.6	9.1	10.9	12.8
B_2H_6 (mm.)	375	366	373	362	367	362
B_4H_{10}[(a)] (mm.)	0.2	0.2	0.1	0.1	-	-
B_5H_{11}[(a)] (mm.)	2.7	3.6	4.4	5.0	6.2	6.3

(a) Calculated using equations of McCarty, et al. [(3)]

TABLE XVI

Pressure of Major Species in Copyrolysis of 1 Atm. B_2H_6 and 50 mm. B_4H_{10} at 100.0°C

Species	Time (min.) 45.0	90.0
H_2 (mm.)	146	246
B_2H_6 (mm.)	659	617
B_4H_{10} (mm.)	9.9	12.6
B_5H_9 (mm.)	7.4	12.7
B_5H_{11} (mm.)	38.6	29.1
$B_{10}H_{14}$ (mm.)	8.0	13.1
$B_{10}H_{14}$ (mg.)	4.9	7.9
$(BH)_x$ (mg.)	1.9	5.1

TABLE XVII

Pressure of Major Species in Copyrolysis of 1 Atm. B_2H_6 and 7.0 mg. $B_{10}H_{14}$ at 100.0°C

Species	Time (min.)			
	15.0	25.0	35.0	45.0
H_2 (mm.)	34.0	54.9	75.8	96.0
B_2H_6 (mm.)	726	705	688	679
B_4H_{10} (mm.)	1.6	2.4	3.6	4.6
B_5H_9 (mm.)	0.1	0.5	1.1	2.2
B_5H_{11} (mm.)	11.5	16.8	20.9	23.9
$B_{10}H_{14}$ (mm.)	10.0	9.7	9.6	10.0
$B_{10}H_{14}$ (mg.)	6.2	5.9	5.9	6.0
$(BH)_x$ (mg.)	1.3	2.2	2.5	4.2

TABLE XVIII

Pressure of Major Species in Copyrolysis of 50 mm. B_5H_{11} and 500 mm. H_2 at 100.0°C

Species	Time (min.)			
	90.0	120.0	135.0	150.0
H_2 (mm.)	473	474	468	483
B_2H_6 (mm.)	89.4	94.0	95.5	97.4
B_4H_{10} (mm.)	5.7	3.4	2.9	2.4
B_5H_9 (mm.)	3.0	3.3	3.4	3.4
B_5H_{11} (mm.)	2.2	1.3	0.8	0.6
$B_{10}H_{14}$ (mm.)	1.5	1.6	1.8	lost
$B_{10}H_{14}$ (mg.)	0.9	1.0	1.1	lost
$(BH)_x$ (mg.)	-	-	-	-

TABLE XIX

Pressure of Major Species in Copyrolysis of 60 mm. B_5H_{11} and 250 mm. H_2 at 100.0°C

Species	Time (min.)		
	60.0	90.0	120.0
H_2 (mm.)	241	240	244
B_2H_6 (mm.)	67.0	74.3	79.5
B_4H_{10} (mm.)	10.0	6.4	4.6
B_5H_9 (mm.)	4.9	5.9	6.1
B_5H_{11} (mm.)	8.1	5.4	4.0
$B_{10}H_{14}$ (mm.)	3.8	4.4	3.9
$B_{10}H_{14}$ (mg.)	2.4	2.7	2.4
$(BH)_x$ (mg.)	1.5	0.4	1.2

TABLE XX

Pressure of Major Species in
Pyrolysis of 1 Atm. B_2H_6 at 126.1°C

Species	Time (min.)							
	2.5	5.0	10.0	15.0	20.0	25.0	30.0	40.0
H_2 (mm.)	34.2	73.3	152	230	303	372	419	498
B_2H_6 (mm.)	709	688	602	561	522	495	468	420
B_4H_{10} (mm.)	1.6	3.0	6.4	8.8	9.8	9.9	9.1	7.7
B_5H_9 (mm.)	0.4	2.4	8.7	15.6	20.8	23.5	26.4	28.2
B_5H_{11} (mm.)	14.2	26.1	31.5	28.4	23.2	18.5	15.4	10.1
$B_{10}H_{14}$ (mm.)	-	1.4	4.8	8.9	12.4	17.1	-	20.2
$B_{10}H_{14}$ (mg.)	-	0.8	2.8	5.1	7.1	9.7	-	11.8
$(BH)_x$ (mg.)	-	-	1.4	2.9	4.6	6.9	-	12.7

TABLE XXI

Pressure of Major Species in
Pyrolysis of 0.5 Atm. B_2H_6 at 126.1°C

Species	Time (min.)		
	5.0	10.0	15.0
H_2 (mm.)	27.8	55.7	86.0
B_2H_6 (mm.)	350	327	298
B_4H_{10}[(a)] (mm.)	-	0.4	1.5
B_5H_9[(a)] (mm.)	-	1.8	5.1
B_5H_{11}[(a)] (mm.)	13.5	19.0	18.1

(a) Calculated using equations of McCarty, et al.[(3)]

TABLE XXII

Pressure of Major Species in Copyrolysis of 0.5 Atm. B_2H_6 and 9.7 mg. $B_{10}H_{14}$ at 126.1°C

Species	Time (min.)					
	4.0	5.0	8.0	10.0	15.0	20.0
H_2 (mm.)	31.0	39.5	63.7	81.4	116	151
B_2H_6 (mm.)	355	348	331	317	294	282
B_4H_{10} (mm.)	0.8	0.8	1.5	2.1	2.9	3.5
B_5H_9 (mm.)	0.5	0.6	2.0	3.0	5.8	8.2
B_5H_{11} (mm.)	8.0	9.0	11.6	13.0	13.0	11.9
$B_{10}H_{14}$ (mm.)	14.6	14.2	13.4	9.2	11.9	12.6
$B_{10}H_{14}$ (mg.)	8.4	8.2	7.6	5.3	6.9	7.2
$(BH)_x$ (mg.)	1.4	2.4	3.9	6.0	7.0	8.2

TABLE XXIII

Pressure of Major Species in Pyrolysis of 1 Atm. B_2H_6 at 140.0°C

Species	Time (min.)						
	4.0	7.0	10.0	15.0	20.0	60.0	10.0[a]
H_2 (mm.)	155	309	428	566	657	951	428
B_2H_6 (mm.)	606	515	455	401	360	231	457
B_4H_{10} (mm.)	5.9	8.8	8.0	6.8	5.3	1.9	7.0[b]
B_5H_9 (mm.)	9.7	23.5	30.8	36.2	38.2	40.1	28.8[b]
B_5H_{11} (mm.)	32.8	24.2	14.8	9.0	5.8	1.0	14.6[b]
$B_{10}H_{14}$ (mm.)	4.2	13.7	19.5	22.2	21.8	12.6	17.0[c]
$B_{10}H_{14}$ (mg.)	2.3	7.6	10.8	12.1	12.1	7.0	9.4[c]
$(BH)_x$ (mg.)	-	3.2	5.7	12.9	17.7	36.7	9.5[c]

(a) 70 mm. cyclohexane present initially.
(b) Calculated using equations of McCarty, et al.[3]
(c) A small amount of $B_{10}H_{14}$ may have been lost during sublimation and weighed with the $(BH)_x$.

TABLE XXIV

Pressure of Major Species in Pyrolysis of 1 Atm. B_2H_6 at 112.4°C with Periodic Removal of H_2

Species	Time (min.)				
	10.0	20.0	30.0	45.0	60.0
H_2 (mm.)	49.8	47.1	51.0	87.8	86.7
B_2H_6 (mm.)	690	645	606	550	516
B_4H_{10}[a] (mm.)	0.8	0.4	0.1	3.0	2.4
B_5H_9[a] (mm.)	-	0.9	5.2	11.2	15.1
B_5H_{11}[a] (mm.)	25.2	38.7	41.1	36.1	31.2
$B_{10}H_{14}$ (mm.)	-	-	-	-	11.4
$B_{10}H_{14}$ (mg.)	-	-	-	-	6.8
$(BH)_x$ (mg.)	-	-	-	-	11.3

(a) Calculated using equations of McCarty, et al.[3]

TABLE XXV

Estimation of the Pressure at Run Conditions of the Unknown Species Obtained in the Copyrolysis of 760 mm. B_2H_6 and 125 mm. B_5H_9 at 112.4°C

Time (min.)	3.0	5.0	10.0	15.0	20.0	30.0	40.0	50.0	60.0	90.0
Total Pressure of Intermediates (mm.)[a]	124	123	120	114	116	113	106	107	104	96
Pressure of B_4H_{10}, B_5H_9, B_5H_{11} (mm.)[b]	113	111	115	110	109	108	103	104	102	93
Δ Pressure (mm.)[c]	11	12	5	4	7	5	3	3	2	3

(a) Determined from pressure-volume-temperature measurements of the total intermediate hydride fraction.
(b) Determined from infrared analysis.
(c) Difference between the two determinations - difference considered to be due to presence of the unknown species.

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